The Journal of the
American Leather Chemists Association

SUPPLEMENT NO. 8
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Report of the
SYMPOSIUM
on
VEGETABLE TANNING

held at the

Fifty-sixth Annual Meeting

of the American Leather Chemists Association

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The Tanning Symposium of the Fifty-sixth Annual Meeting of the American Leather Chemists Association was held on Wednesday morning, June 22, 1960, at the Lake Placid Club, Lake Placid, New York.

INTRODUCTION

CHAIRMAN JOHN F. WAGONER

Armour Leather Company
Williamsport, Pa.

The theme of our symposium this year is The Role of Vegetable Tanning in Today's and Tomorrow's Leather.

All of us take just pride in the antiquity of our vegetable tanning processes. We are prone to brag about the length of time and the delicate care that is required to bring out the esthetic qualities of our leathers. Today, we are encountering the stiffest kind of competition from synthetics and plastics. Therefore, we need to exploit to the fullest extent the technical advancements that have been and are being made in our industry. We who are in production and development work must continually reappraise the technical aspects of tanning in the light of new and existing scientific knowledge in order to operate our processes as efficiently as possible and to produce and develop leathers with quality characteristics that will be marketable at a profit.

We hope, here in the course of our discussions this morning, to point up pertinent and practical applications of vegetable tanning that will be helpful to all of us, not only in our day-to-day production but also in our new leather developments.

To bring this subject of vegetable tanning into proper focus perhaps it would be well to consider first the scientific principles involved. Therefore, to learn what we are doing, we will go to our first paper.

THE SCIENTIFIC PRINCIPLES OF VEGETABLE TANNING

ARTHUR N. KAY

Howes Leather Co., Inc.
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While the preservation of raw hides and skins by the action of vegetable tanning materials is a comparatively simple matter, the practice of leathermaking—our primary interest—is exceedingly complex. Not only must the raw stock be converted into an imputrescible material, but that material must also have imparted to it many other properties to make it suitable for the particular end use to which it is to be put. Then, and only then, can the product be considered leather.

Since the raw stock is a protein, its behavior and properties are determined by its environmental history, and this must always be kept in mind when considering the factors influencing any particular phase of the over-all process.

Before we can discuss the scientific principles of the isolated phase of vegetable tannage, it is equally essential to remember that the accent is on *principles*. These *principles* are always operative, but they are so interrelated and so interwoven with those of the prior and subsequent phases that, in practical leathermaking, it is only rarely that the specific effect of any one is readily discernible. Rather, as practical tanners, we are concerned with maintaining a delicate balance among the many factors involved.

The advantage of considering the individual factors is, of course, that one is the better prepared either to maintain an existing balance in the face of necessary changes in raw materials, process changes made for economic reasons, and the like, or to strike a new balance when changed market conditions demand a new end point.

Insofar as actual vegetable tannage is concerned, the factors to be considered are: type or types of tanning material used, time, temperature, concentration, viscosity, degree of dispersion, type and amount of acidity, pH, neutral salts, and the solvent used. For the purpose of this introductory survey, these can only be considered in the most general terms.

Tanning materials.—These may be conveniently divided into two groups. The *catechol* tannins tend to be reddish; low in acidity, sugar, and salts; and high in insoluble matter. Their solutions are very sensitive to pH changes, readily precipitating further insoluble matter when the pH is lowered. Penetration is slowish, but the leather tends to be full and firm. When treated with (usually) sodium bisulfite to eliminate the insolubles, they become relatively nonastringent, rapidly penetrating, but giving flat and empty leather unless the acidity be suitably modified. The *pyrogallol* tannins tend to be

yellow to brown, high in acidity (partly from free organic acid, partly because their tannins are themselves acids), with a fairly high sugar content. Some, notably sumac, are highish in neutral and buffer salts. While initially tending to be low in insoluble matter, many tend to deposit "bloom" as a result of enzyme action. Penetration is usually slow, although, at least in the case of chestnut, this can be modified by various "sweetening" procedures.

In addition to the vegetable tannins proper, it is also necessary to consider the lignosulfonates and the two major types of syntans, as these are being increasingly used. For the immediate purpose it is perhaps sufficient to consider the lignosulfonates and the auxiliary syntans together; while both tend to be low in insolubles, rather insensitive to pH changes, and high in neutral salts, they are not leathermaking materials as such but, rather, are additives to be used with, or to modify, the more usual materials. The replacement syntans are true leathermaking materials, usually rapid penetraters, low-yielding, highish in neutral salts. The various types of tanning material are usually blended to strike a suitable balance for color, rate of penetration, yield, plumpness, and solidity desired in the finished leather.

Time.—Other things being equal, the greater the time the more uniform the distribution of tannin throughout the thickness of the hide and, usually, the firmer the resulting leather.

Temperature.—Increasing temperatures tend to increase rate of penetration and increase fixation, producing firmer, plumper, and heavier-yielding leather.

Concentration.—Other things being equal, the higher the concentration the greater the rate of penetration and the amount of tannin fixed, and the firmer the leather. However, viscosity, degree of dispersion, and the astringency are also increased, and a point is soon reached where penetration begins to fall off and where the tannin fixes on the outside of the fibers and, later, "grabs on" so violently that penetration ceases (casehardening) unless modifications are made by the use of syntans, salts, etc.

Viscosity.—While the different materials differ in viscosity, at the temperatures and concentrations normally used it seems probable that this is not too great a factor, although some experimenters feel otherwise. My own feeling is that surface, or rather interfacial tension, may be more significant.

Degree of dispersion.—This is not well understood, largely because no dependable method for studying particle size has yet been developed. Indirect evidence suggests that the smaller the particle size the more rapid the penetration but the lower the degree of tannage, weight-yield, and plumpness.

Type and amount of acidity and of pH.—While increasing the titratable acidity and lowering the pH both tend to make plumper, firmer, and redder

leather, neither alone is sufficient to characterize a particular situation in the tannery. With the stock usually carrying a certain amount of alkali (lime) from the beamhouse, the liquors must have a sufficient reserve of titratable acidity to control the pH within the limits found desirable. The weaker the acid present the greater its dispersing (therefore plumping) action on the hide at any given pH value, while there is some evidence that hydroxy acids have a greater tendency to plump and to fix tannin than do the non-hydroxy acids of similar pH value. The sequestering power of the hydroxy acids is usually greater, and this is important from the standpoint of controlling stains.

Neutral salts.—These act oppositely to acidity and pH: that is, as they are increased the leather tans more uniformly and quickly and is less plump, softer, and lower-yielding, while the color tends toward the yellow side. Not much work has been done on the effect of different salts, but sulfates seem to have a greater effect than chlorides. It is my own feeling that the effect is related to changes in the swelling of the hide and in the degree of hydration of the tannins.

How these various factors are balanced in actual leathermaking practice will be discussed by the other panelists. As a general summary, however, rocker tannages use a blend of pyrogallol and catechol (usually "solubilized") materials to get the desired color, solidity, and rate of penetration consistent with economy; such a blend is run countercurrent to the stock so that the untanned hide first meets the least astringent tannins in the presence of highish neutral salts and minimum acidity and then progresses through stronger, more astringent, and more acid liquors. Lignosulfonates and syntans may form part of the blend where specific effects are wanted.

In wheel or paddle tannages, the tendency is toward previously delimed or even pickled stock, thereby reducing the need for buffered acidity. Concentrations are comparatively high, but viscosity and astringency effects are offset by the increased mechanical action, by the use of salts, and by the use of syntans. One trend for the future seems to be in the direction of increased use of wheel and paddle tannages, even for heavy leathers. Pretannage of the raw stock with rapidly penetrating materials, such as aldehydes, syntans, and mineral tanning agents of various kinds, followed by retannage in short rockers or even in the wheel, is being increasingly investigated in order to meet the demand for lighter-weight, more flexible leathers produced more economically and for keeping production closer to the market.

Lastly, we must consider the solvent used. In the foregoing, water has been the normal solvent—as it has been since recorded history began, and probably before that. While water has had many advantages, it has also had many disadvantages, not the least of which is that it wets and combines with the hide and hydrates the tannin so that the latter must diffuse through

a layer of adsorbed solvent, and the product tends to be overtanned on the surface and undertanned in the interior. If this self-limitation were not enough, the increasing scarcity of this solvent for other purposes should compel us to consider alternative solvents. Once we thus cease to limit our progress, a whole new horizon is opened up. It is well known that the amount of preservative needed to render hide chemically stable (i.e., imputrescible) is but a fraction of that normally employed—provided that it can be uniformly distributed throughout the hide.

Further, while some of the conventional tanning materials are soluble in other solvents, there is a whole host of useful materials which are *only* soluble in nonaqueous solvents. Many such are either relatively simple mixtures or even single entities, thereby, in large measure, eliminating the variables inherent in the use of water-soluble, "natural" materials, while many of the factors so important in aqueous tannage are either minimized or eliminated entirely. The physical stability of such leathers can be obtained more quickly and more cheaply by use of suitable impregnants whose presence can yield leathers with properties superior to those of more conventional tannages.

It seems to me highly probably that solvent tannages are those of the future, the more especially if "reconstituted hide"—the dream of leather chemists—can be brought to practical reality, and there is considerable evidence that this may soon be the case.

CHAIRMAN WAGONER: Now let us see how these principles are being applied under our present conditions and what is in the offing. We start first with a presentation by Richard N. Jones of A. C. Lawrence Leather Company.

VEGETABLE TANNING OF SHEEPSKIN LEATHER

RICHARD N. JONES

A. C. Lawrence Leather Company
Peabody, Massachusetts

Today vegetable materials are used extensively in the production of many sheepskin leathers. They probably find their greatest usage as retan materials in chrome-vegetable combinations, but they are still used to some extent as primary or sole tannages. Sheepskin leathers manufactured by such processes include shoe and boot linings, hatbands, bookbindings, and certain specialty leathers for ladies' and men's wallets, diploma cases, and the like. The filling and firming characteristics of vegetable tannins lend themselves well to the production of these—the so-called firm end of sheepskin leathers. In addition to these properties the tan process must be designed to produce a smooth, crack-free grain.

For the most part drum tanning is practiced nowadays, the exception to this being skivers which do not possess the necessary strength to withstand the pounding in a drum. Accordingly, my remarks will be based on the drum tanning of domestic and New Zealand wool-type sheepskins from the pickled condition.

Because the raw stock in question is loose and open in fiber structure, it is certainly desirable to keep drumming time to a minimum. Otherwise the physical stresses and strains which accompany excessive drumming may detract from the end result by producing drawn grain or double-hided leather. The optimization of a sheepskin vegetable tannage, therefore, centers about the following: execution of a thorough tannage which produces the maximum of desirable leathering effects in a minimum of running time. The chosen process must be economical. A wide operating range in the variables important to vegetable tannage is apparent if one reviews past and present practices in our industry. Consider, for example, the following succession of steps followed in a typical process, noting the fluctuation in methods or amounts employed.

1. The pickle skins are first degreased. The degreasing process may be thorough, leaving 3 or 4% grease, or it may be mild, leaving as much as 10% grease on the dry weight.

2. The brine float in which the skins are drummed prior to the feeding of the tan may vary from 75 to 150% on the pickle weight; its salt concentration, from 4 to 7%.

3. Adjustment of the pH, which, depending upon the degree of pickle, may vary over the 1.5 to 3.0 range, is often undertaken at this point; at other times it is ignored.

4. There are obviously a multitude of possible extract combinations which can be employed. They may contain or be preceded by moderate amounts of syntans or lignosulfonates. From 35 to 60% of liquid extract is used.

5. The feeding time of the extract is sometimes rapid—for example, one-half the total amount for 30 minutes, the remainder added and drummed 2 or 3 hours. Or it may be fed slowly, as 25% portions of the total spread over a 2-hour period, with the final feed running a couple of hours. And, finally, a compounding of these is sometimes used, that is, unequal feed portions at varying time intervals. pH adjustments may or may not be made near the end of the running time.

6. The skins are sometimes horsed up at this point, or they may be allowed to lie at rest in the tan wheel overnight. After fleshing, a vegetable retan may or may not precede the coloring and fatliquoring.

A common variation in the order of steps mentioned above calls for striking the pickle stock with a small amount of extract at the completion of the degreasing. The skins are fleshed at this point, and the tanning, coloring, and fatliquoring are then accomplished in succession in the same wheel.

We have heard Mr. Kay discuss the scientific principles of vegetable tanning. In light of this I should like to pose a few questions with respect to the sheepskin process variations just enumerated.

First of all we have the degreasing. Is enough attention paid to this initial operation which will exert some influence on the tannage to follow? Naturally, we don't want greasy skins on the finish table, but are we sometimes prone to overgreasing? For certain leathers, I believe we are.

Secondly, there is the matter of salt concentration in the brine solution prior to the introduction of the vegetable tan. We are told that salt, especially at low pH levels, has a marked effect in reducing tannin fixation. Aside from this consideration, and again related to conditions of acidity, is its effect on the degree of swelling—or in other words, the condition of the fibers when they receive the tannin. Doesn't it follow, then, that a given tannin will produce its maximum filling and plumping effect when the salt concentration is kept to a minimum, thereby promoting greater fixation on a fiber structure whose swelling tendency has not been overly depressed?

A third factor is pH. This has added significance if the tanner is using rawstock from several different pulleries and consequently of different degrees of pickle. The extent to which variation in pH at this point levels out after addition of the extract depends somewhat on the acidity of the tannin itself. Any such levelling out, however, certainly does not come about in-

stantaneously, and I suggest that to ignore this variable is to invite non-uniformity from pack to pack. Besides this, pH is certainly a valuable tool by which the rate of penetration can be altered.

The factors mentioned to this point have to do with conditioning the goods for receiving the tan. Since the tanner has little control over the beamhouse operations his rawstock has been subjected to, they are certainly most deserving of his careful control so that the tannage will be applied to uniform stock.

We come next to the selection of the extract or blend of extracts. Quebracho is the workhorse; it is used to some extent alone, but also as the starting point around which blends are formulated. It possesses good filling, is firm, has a noticeable reddish cast, and is poor in lightfastness.

The addition of wattle, in an amount up to 50% of the quebracho used, has a mellowing effect on the resultant leather and throws the color toward the greyish cast. The addition of moderate amounts of sumac reduces the astringency of the blend and promotes softer leather. Chestnut can be added when additional solidity is called for. Instead of compositing the properties of different extracts into one blend the tanner may initially feed a blend containing a higher proportion of the less astringent materials and complete the tannage with one formulated in the opposite direction. By and large, the properties of most sheepskin vegetable-tanned leathers can be attained by the use of quebracho and wattle, and because of price or availability other materials find only extremely limited use.

Vegetable blends are often further modified by the addition of auxiliary or replacement-type syntans. Improved penetration, clarity of color, and grain smoothness are some of the virtues attributed to their use. A question to be considered here is whether they have a more pronounced effect in altering these characteristics if used as a pretan rather than incorporating them in the vegetable blend.

To the best of my knowledge the extent to which lignosulfonates are used in sheepskin vegetable tannage is still quite limited. They have a place, but in our laboratory their role has not been completely resolved. Their use to replace a portion of the vegetable extract must be evaluated separately on each extract blend used. For example, you cannot indiscriminately say that X amount of lignosulfonate will replace Y amount of extract; it differs considerably with the nature of the original blend.

In considering the method of application of the tan material we think first of the concentration. After the initial brine float is regulated, the concentration of the tan liquor is controlled by the number of extract feeds and how far apart they are spaced. Concentration plus another controllable variable, namely, temperature, will affect the dispersion of the tan and particle size. These factors, in turn, influence the rate of penetration and tannin fixation, the items which are of ultimate interest to us. Their control is obviously

important in the interests of minimum drumming time commensurate with producing quality leathers. Just what are the optimum conditions for striking a balance between penetration and fixation? To be specific, will a tighter, better-filled, smooth-grained leather be obtained by (*a*) 25% feed portions over well spaced intervals, or (*b*) an initial 25% feed followed closely thereon by the remaining 75% and reducing running time?

Finally, the over-all length of tan time—that is, whether or not to leave the stock at rest in the tan liquor overnight—must be considered. Some tanners hold that the added cost of a vegetable retan during the coloring and fat-liquoring operation is actually more economical in terms of better leather quality.

In conclusion it should be mentioned that interesting sheepskin leathers are produced by retanning on top of vegetable with chrome, zirconium, and aldehydes. It is my opinion that this area holds the greatest future potential for sheepskin vegetable tannage, as such modified tannages are capable of producing leathers which fit into the trend toward a softer, more mellow product.

VEGETABLE TANNING OF UPHOLSTERY LEATHER

ELWOOD E. PRESLEY

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The role that vegetable tanning plays in the production of upholstery leather is very similar to that for sole, bag, and case leathers. The physical requirements for upholstery leather are somewhat different from the above, so a slight description of just what is required is necessary.

Up until the last few years a leather that was fairly solid, supple, and strong, yet readily worked with the assistance of some softening by means of plain water, was sufficient for upholstery use. With the advent of pastel colors and high styling, drapey, mellow, full round-feeling upholstery leathers, with a strong grain was more in order. All upholstery leathers are produced to meet the specifications of the Upholstery Leather Group. The latest revision was made in 1958. The upholstery tanners supplying the automotive and aircraft industry have additional requirements. The requirements of these two groups are very numerous, as one can well imagine if he has had any dealings with them, especially the automotive people. Their methods consist of a series of physical tests on both the leather and the finish.

One might imagine that vegetable tanning would only have a bearing on the feel and physical strength of the leather, such as breaking strength, stretch, and stitch tear. This is far from being entirely correct. Vegetable tanning shows its influence on the following finish tests: fadeometer exposure; South Florida exposure; sun, oven, and steam yellowing tests; bleeding; and resistance to perspiration. Certain tannins as well as uncombined tannins that are free to move around due to the ever present moisture in leather can cause considerable trouble on light-colored leathers in the presence of ultraviolet light rays. These facets will be taken up later.

Before upholstery leather can be vegetable-tanned into a satisfactory product, proper pretreatments are vitally necessary. To mention the process briefly will suffice.

First, the green-salted hide should be thoroughly wet back to its original state before being green-fleshed to remove fat, flesh, and some tissue for a better liming process. A 4- or 5-day mellow lime will open and plump the hide sufficiently so that the hair can be easily removed and reclaimed. The long mellow lime insures minimum protein degradation and rupturing of the fibrils and fiber bundles. This is all to obtain maximum physical strength. A complete deliming by a long bate and layover in water overnight before entering the tan yard prepares the hide for the subsequent vegetable tanning.

I do not mean that the above procedure is the only way to produce upholstery leather. It is the conventional method of pretreating the vegetable leathers. Today, due to the necessity of shorter time in process and smaller inventories for economic reasons, satisfactory upholstery leathers can and are being produced from a hair burn-off system, followed by lime splitting, pickle, chrome tan, and then a vegetable retan. For the moment, however, let us consider the conventional method of vegetable tanning upholstery leather.

The conventional tan yard tanning principles are very similar to those described by my predecessor, Mr. Kay. The first-day tannage consists of a low-tannin-content liquor, 0.9 to 1%, at 68°–72° F., and pH around 5.0. Each day the liquors are gradually increased in tannin content and lowered in pH value. The increase in tannin will depend upon the total time in the yard. Eight-to-12 vat sections are being used for the most part. The head vat liquor usually contains 3.5 to 4% tannin with a pH of 4.2–4.4.

A low-tannin-content liquor should come in contact with the raw hide first. The tannin will combine slowly with the grain and flesh but still permit penetration of more tannin as the heavier liquors are pressed onto the section. If a high-tannin-content liquor comes in contact with the fresh hide, the surface becomes tanned too fast and reduces the penetration of tannins. This is called casehardening. When this occurs, the corium or fibers are not properly tanned. Extra care in the subsequent vegetable retannage is therefore necessary.

Insufficient tannin can cause a variation in splitting which may result in a waste. For example, you are splitting a properly tanned hide out of the tan yard at 3 ounces. A casehardened hide will split about the same, but in retanning the hide will plump up due to tanning of the fibers. This hide will therefore have to be shaved down, which is a loss of leather and entails additional labor cost. As this particular hide is not plumped properly in the first tan, the deep buff will be undertanned as well and will show the same plumping after splitting, thereby requiring shaving and more unnecessary hide loss. Having already taken off two splits with wasted amounts of leather substance, this can only mean one thing, a lighter-weight insole slab. The additional weight the latter should have had, has been lost in the shaving operations.

pH control is necessary to assist the tannin to penetrate the hide. With sufficient acid to reduce the inner pH of 7.5–8.0 after bating to the 4–5 pH range appropriate for tanning, the tannins will penetrate the hide. Without this acid the tanning process is materially slowed down.

Tannins penetrate better in a warm medium. Tannin penetration in the yard is always better in the summer than during the winter months. During the latter it is good practice to pass the head liquors through a heater and carry the new make-up liquor at a higher temperature to keep the average temperature of the tan yard up to its optimum tannin penetration point.

The tail liquor is, in a sense, the most important liquor in the section and sets the stage for the final characteristics of the leather. If too much lime is repeatedly carried over into the tail liquor, dark, smelly liquors and leather result. The tail liquor can be governed by proper control of the bating process, daily sewering of sufficient tail liquor, and pH control. The latter can be done with the use of sulfuric acid, lactic acid, or hydroxyacetic acid. We find the latter an excellent material to use for this purpose. The amount to be used will vary from 2 to 5 quarts per rocker daily, depending upon the particular quality control system.

The vegetable tannins usually used are a mixture of catechol and pyrogallol. For years we ground and leached our own hemlock bark to use as a base liquor. With the diminishing of the easy supply from Michigan's Upper Peninsula and increasing costs of both the bark and upkeep of the leachhouse equipment, we have stopped this operation. Quebracho comprises the majority of the extract blend. It is bisulfited to solubilize some of the insolubles as well as nontannins into useful tanning products. The use of hydroxyacetic acid and alum during the final stages of the bisulfiting governs the pH and the color of the extract.

Wattle extract is occasionally substituted for part of the quebracho. Ten to 20% can be used to satisfaction. Its assets are that it is less astringent, contains a fair amount of sugars and nontannins, and is low in insolubles. The penetration of the wattle tannin is rapid and less susceptible to pH change. Treating wattle with citric acid can produce an excellent replacement for chestnut.

The above-mentioned extracts are catechols and are characterized by yielding reddish leathers. They contain very little acid or sugars, and their solutions are very sensitive to pH change, yielding a precipitate of phlobaphenes or "reds" upon acidification.

In blending extracts with base liquors it is a good rule to have all the components at approximately the same temperature, no more than 10° F. difference. This reduces the precipitation of insolubles or reds during the blending.

The pyrogallol-type tannins used for their acidic nature, color, and less tendency to form reds, are chestnut, oak, myrobalans, and valonia. With the loss of the hemlock bark and with the prohibitive costs of some of the catechol tannins, we have found that Orotan TV is a very satisfactory replacement or exchange tannin. It imparts strength to the leather, does not cause casehardening, offers considerable pH control, speeds up tannin penetration, prevents raw spots, and yields a lighter-looking russet leather. It is, however, more expensive and has caused some storage problems due to its acidic nature.

After splitting the full hide into a grain, deep buff, and insole slab, the individual splits are given a vegetable retannage with the same materials. In the case of incomplete tannin penetration due to heavy hides or kiss marks in the tan yard, a day's immersion in Orotan solution will complete the tannage without injuring the practically raw fibers.

As a means of economy some lignosulfonates and syntans can be used in small amounts in the blend in the original tanning. If the tan yard is designed so that the tail liquor can be treated separately, the use of syntans at this point is often advantageous. A smooth, clean grain, light color, and rapid penetration of tannin from subsequent full liquors can be the result of this pretannage.

Vegetable tanning of upholstery leather is simply a series of adjustments: the proper tannin blend, control of the pH, temperature, and governing the tannin content of the liquors to obtain the greatest penetration. The rules are very simple, but a great deal of know-how and practical experience is necessary.

So far we have covered the conventional method of vegetable tanning upholstery leather. A rapid method of producing upholstery is to lime-split, pickle, and pretan with a syntan, formaldehyde, lignosulfonates, or chrome prior to vegetable tanning with extract blends. Great care must be exercised to prevent drawing and milling of the grain. Loss of area can result if improper balances of the above factors are not watched. A decrease in physical strength is always a possibility.

In rocker yard tanning, the tannin blend, pH, temperature, and tannin content were important variables to be controlled. During the rapid method of vegetable tanning, these same variables are important, but they are controlled somewhat easier. The blend is chosen for its color and the influence it exerts in producing maximum physical strength. The pH of the stock is already in the proper tanning range due to the pretan. Usually, a buffer salt is added to control the presence of mineral acids. The temperature can be controlled by the speed of the tan drum, time of running, or the amount of float. Tannin penetration is faster due to heavy mechanical action. Case-hardening is less important here due to the leather being split, mechanical action, and higher tanning temperatures. The extract blend can also be added in small increments to reduce heavy tannin fixation on the surface.

In my introduction I mentioned ultraviolet exposure tests which were affected by the vegetable tannins. Finished upholstery leathers made by the latter method show increased resistance to color changes due to the tie-up of tannins and nontannins by the special pretannages. Despite the presence of a 2- to 4-mil thickness of finish material, certain tannins can create havoc on light-colored finished leathers when exposed to heat and UV.

Solvent vegetable tanning is still in the future for upholstery leather. Very satisfactory upholstery leather can be made, and has been made, by this method, but to date no method has been devised which has an economic advantage. The equipment for safely processing solvent-tanned hides is available. It is just a matter of time to work out an economically advantageous system. New tanning materials and auxiliaries are being produced yearly. By combining equipment, newly developed materials, and scientific knowledge of the complex structure of the hide, solvent-tanned vegetable leather could be a competitive commodity.

VEGETABLE TANNING OF BAG, CASE, AND STRAP LEATHERS

C. A. Lauder

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Tanning of bag, case, and strap leathers has been an art in North America for at least a century. Tanners with foresight built their small tanneries near the hemlock forests in the eastern United States and Canada because tannin from the hemlock bark was all they required to tan fine leathers.

Chemists were little known in North American tanneries in those days, as control of tan liquors was relatively simple. But as the hemlock forests dwindled and the bark became scarcer, tanning barks and extracts of other origin had to be used. As tanning became more complex there was a need to employ technical personnel in the tanning industries. Today, sufficient technical personnel is the mark of a progressive tannery.

In northern Argentina and southern Paraguay grows the mighty quebracho tree. Strange as it may seem, the tannins are found in the heartwood, the wood at the center of the trunk and not in the bark. Quebracho wood is one of the hardest woods in the world. Its name means "break axe". The tree grows very slowly, and it is said it must be 100 years old before it is felled to produce one of the world's most valued tanning materials. Some trees that are felled are very close to 500 years old.

The quebracho extract produced is usually bisulfited by the extract manufacturer or the tanner. We know of no tanner using regular quebracho that has not been bisulfited, for unbisulfited quebracho penetrates the hide too rapidly, is very astringent, and would cause the grain of the leather to draw and pebble. Poorly bisulfited or unbisulfited quebracho liquors would be very cloudy at tanning temperatures, and the blended liquors in the yard would have an excessive amount of sludge.

Bisulfited quebracho, by itself, produces a rather flat, empty leather. Therefore, as the supplies of hemlock became meager, it was necessary to add other tanning materials.

Myrobalan tannin was introduced in small percentages to add sugars which would ferment and produce organic acids in the tan liquors. This type of tanning material is known as an acid former. It produces somewhat softer leathers of lighter shade.

Wattle tannins were used to replace hemlock. They produce a light pink tan and tend to plump and fill the leather more than bisulfited quebracho. Wattle liquors contain a higher percentage of nontannins than do bisulfited

quebracho and consequently are lower in purity, as they penetrate the hide more rapidly. They sometimes are bisulfited slightly, but only for reasons of color. A good supply of wattle extracts is assured so long as the sea lanes are open, as the wattle trees grow very rapidly and produce a good grade of tannin. The trees are planted and harvested in South Africa.

European chestnut extracts, French or Italian varieties, are used to impart firmness into the leather. They assist in giving a flat, smooth grain surface on vegetable leather and give a light yellow-brown tannage. Their tannins penetrate rather slowly, producing leathers that are well filled.

Some oak tannage for bag, case, and strap leathers is carried on in California. Oak tans impart a yellow-brown color to the tannage, darker than European chestnut. The leather is well filled and not too firm. The tans penetrate fairly slowly.

Valonia extracts, like myrobalan extracts, are acid formers. They, too, should only be a small percentage of the total blend, for in larger quantities either of these extracts may cause sludge to form in the tan liquors. They should not, in our opinion, each form more than 5 to 6% of the blend. In small quantities they do not appreciably affect the color of the tan. They help to give firmer, well filled leather. Valonia comes from Turkey.

Sumac extract is used principally for retanning. It imparts a mellow, soft feel to the leather, especially to the grain.

These principally are the extracts which may be used in a blend to make bag, case, and strap leathers. However, the use of blends makes tanning more complex, and the system, therefore, requires close chemical control. And that is where the technical man, the chemist, comes into the picture.

A tanning system for bag, case, and strap consists of a series of vats, 6, 8, 10, or 12 in number, of different liquor strengths, the head vat having the strongest liquor and the tail vat the weakest. These liquors are tested by a type of hydrometer known as a barkometer. Usually the barkometer of the head vat is 30°–36° (sp.g. 1.03–1.036) and the tail vat is 12°–17° (sp.g. 1.012–1.017). The tan liquor blend is run into the head vat of the series daily, and this run presses the liquors in the other vats to the tail vat where the overflow of weak liquor runs into the sewer.

The bated sides from the beamhouse are tacked into the tail vat on sticks and are moved regularly every 2 or 3 days toward the head vat. They remain in the head vat until they are tanned, at which time they leave the tan yard for further processing.

The vats in between the head and tail vats will gradually reduce in regular order in barkometer and increase in pH from the head vat to the tail vat. This order is assured by testing and analytical control. A tannin analysis is taken at regular intervals to control the purity of the liquors. Total acidities are also taken regularly to maintain enough acid in the tail end of the system to neutralize the lime left in the hides after the beamhouse process. It is

very necessary to assure that the required amount of total acid is in these liquors, as experience has shown that decomposition can take place if insufficient acid is present. Total acidity and pH are not necessarily related, as acids of different strengths will be present.

If the tail liquors are found to contain too little acid, then lactic acid or hydroxyacetic acid is added. Either of these acids will firm up the leather and tend to lighten the shade.

A good pH for the tail liquors is 4.7–4.9, and for the head liquors, 3.9–4.0.

Where the right proportions are used in the blend and the counterflow system is closely controlled, a fine grade of bag, case, and strap leather may be made. This leather would be mellow, yet full of life. It would have a degree of tannage of anywhere from 58% to 65%, usually approximately 60%.

It would make fine leather luggage, wallets and billfolds, attaché cases and portfolios, and bookbinding and waistbelt leathers. It also could be sold for tooling and carving leathers.

It is our opinion that pickling, pretanning, and vegetable tanning of side leather will not produce as fine a quality of bag, case, and strap leather as will the counterflow system in the tan yard.

If we are misinformed, we would certainly like to hear about it.

VEGETABLE TANNING OF SOLE LEATHER

JOHN F. WAGONER

Armour Leather Company
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Leather for use as a shoe-bottoming material must provide comfort, safety, and durability for the shoe wearer. It must have a degree of flexibility and be adaptable to changing shoe styles. It also must have shoe factory workability and meet the process requirements of the various types of shoe construction carried out in shoe factories. Sole leather tanned by the vegetable tanning process can and does meet these requirements.

The vegetable tanning of sole leather can be considered under two main categories, namely, the selection and preparation of the tanning materials, and the operation of the tanning process.

The principal tanning materials used in tanning sole leather are quebracho, wattle, mangrove, cutch, chestnut, myrobalans, and valonia; also syntans and lignosulfonates. The tanning properties of each of these materials are well defined in the literature. Tanning materials are purchased either as extracts or as the raw materials. In the latter case the tanner does his own leaching. It is the general practice to use a blend of several of these materials to obtain the desired fullness of tannage, color, solidity, flexibility, and a minimum time of tannage. The availability of materials and cost also have to be considered. The quality characteristics imparted to the leather are always the balancing factor in regard to the use of a more or less costly material. Other factors to be considered are sludge-forming properties with the resultant loss in tannin, stability, acid characteristics, color, and ease of handling.

The actual blend of tanning materials can be varied quite widely, but today it is the general practice to use a larger percentage of the catechol type of tannins. Thus, quebracho, wattle, and cutch may make up from 60 to 70% of a blend, while the pyrogallol type of tannins, such as chestnut, valonia, and myrobalans, are used to make up the balance. The use of foreign chestnut extract in place of the domestic chestnut extract which is no longer available has resulted in the tanning being carried out in less acidic and higher-purity liquors. This has actually helped in reducing the time required for tanning. Lignosulfonates are used in the blend by some tanners because of their comparatively low cost. They are used in place of part of the chestnut, valonia, or myrobalan extracts and effect a decrease in the purity and a more acidic condition in their liquors. Syntans are used for their solubilizing effect and aid in increasing the rate of penetration. The blending of the tanning

extracts and the mixing of the tan liquors require careful handling to avoid tannin losses and the production of off-color leather.

In preparation of the extract blend the ordinary quebracho is first treated with sodium bisulfite to solubilize the insolubles. This treatment also makes quebracho tan faster. Factors to be considered in bisulfiting ordinary quebracho are time, concentration, temperature, percent bisulfite, and tank construction.

By the addition of 3 to 4% of sodium bisulfite, based on the weight of quebracho, to the dissolved extract, and by maintaining a temperature of 205° F. for 24 to 36 hr., a good solubilization can be obtained. When using cutch in the blend it is considered good practice to add it directly to the bisulfited quebracho and thus obtain some advantage from the bisulfite present. Temperatures above 170° F. are avoided in dissolving and blending wattle extract. Higher temperatures will cause a darkening in color. Powdered chestnut, valonia, and myrobalans are not heated over 150° F. when dissolving and blending. Temperature controls are maintained on the bisulfiting and blending equipment to assure uniformity in the preparation of extracts.

To keep the formation of insolubles in the tan liquor to a minimum it is general practice to build a liquor up with the concentrated blend of extracts rather than to cut a concentrated extract down to the desired liquor strength. The higher the solids concentration of the liquor to which the concentrated blend is added, the lesser the formation of insolubles. Therefore, in the liquor mixing it is best to add the blended extract as the last item. It should be added rather slowly with continuous agitation and at a temperature of approximately 100° to 110° F.

The well-known rocker tanning process is probably the most widely used for the production of sole leather in this country, although a combination of the rockers and layers or a combination of the rockers and drum is also practiced to some extent. During the past ten years or so there has been a marked reduction in the time required to tan sole leather. This has been accomplished by the use of stronger liquors, higher temperatures, circulation of the liquors, a larger percentage of the catechol types of tannins in the blend, and the use of less acidic tan liquors. To produce satisfactory sole leather in the shorter periods of time, the tanner is required to exercise much closer controls on the process to assure uniformity of product. The tanner has learned that uniformity of the tanning blend, uniformity of extract handling, and uniformity of tan yard operations are necessary to maintain quality and to control costs. The practice of continuously changing the extract blend whenever a so-called good buy on a certain tanning material comes along is no longer considered good practice. In the long run it is better to establish a good blend and then stick to it.

The use of tanning extracts permits the tanner to use much stronger liquors in his rocker yard operations. Tannin contents of 8 to 15% in the head rocker

liquor are not uncommon. With these stronger liquors more careful manipulation of the liquors is necessary to avoid undue tannin losses. The inclusion of a large percent of non-acid-making extracts (quebracho, wattle, and cutch) in the blend necessitates more careful adjustment of the pH of the liquors. The tail liquor will carry a pH value of 4.5 to 5.0 and require daily adjustment with acid. Sulfuric acid is commonly used for this pH adjustment, although some tanners prefer lactic acid. The head rocker liquor pH value is often up to 4.0 to 4.3. By circulating and heating the top three or four liquors in a rocker section the rate of tannage is accelerated, and this practice along with the less acidic condition has permitted the elimination of the layer yards in a good many tanneries.

The leather industry operates on a low-profit margin, and therefore costs are always a dominant factor. Considerable cost savings are possible in the vegetable tanning operations. At one time it was common practice to make up the new liquor for the rocker section the same strength every day and then add a volume of liquor to the section equivalent to the volume of liquor sewered. Today the same amount of tannin is added to the section every day, and the strength of the liquor is changed to coincide with volume of liquor being sewered. This not only avoids build-up of tannin inventories in the rocker yard but also helps in producing more uniform leather. Sludge recovery is also more widely practiced, and here it is a matter of recovering the liquor surrounding the accumulation of insolubles in the bottom of the vat. With the present use of stronger liquors this becomes more of a tangible cost factor.

The leather industry is always striving to develop new methods of tanning that will produce leather with improved characteristics and/or reduce the costs. The sole leather tanners are no exception. A good deal of research and development work is continually being carried out on process and product improvement. Considerable work has been done on the possibility of producing sole leather by a drum process, to effect considerable reduction in tanning time.

One of the big problems has been to overcome the tendency of heavy hides to draw or pebble on the grain during the drumming operation. The use of pretanning agents is advocated as a means of overcoming this condition. Such pretanning agents as syntans, lignosulfonates, glyoxal, dialdehyde starch, chrome, and zirconium have been mentioned frequently in the literature. The application of a pretanning agent, followed by vegetable tanning in heavy liquors, usually in a rocker, is also advocated. To the speaker's knowledge, none of these procedures is used to any large extent in commercial practice. However, as more is learned about the technical aspects involved some such procedures may well be the vegetable sole leather tanning process of the future.

DISCUSSION

W. A. Wachholtz (Arthur C. Trask Co.): I would like to ask the panel if they would care to comment on the use of spray-dried extracts compared with extracts made from solid extract and liquefied.

Not too many years ago the introduction of spray-dried quebracho met with some difficulty from some tanners inasmuch as they felt the spray-drying process polymerized the extracts to the point where penetration was difficult and the leather reportedly was harsher. Today with imported spray-dried extracts we find that the comment is that we get faster penetration, a lighter color, and in the case of some of the catechol-type tans, better lightfastness. I would like to know if the panel has had any experience, or if members have any comments to make, along these lines. In other words, what have the results been in the use of spray-dried extracts compared with the use of solid extracts liquefied?

Mr. Kay: I think one point might be taken up—your statement regarding the difference between spray-dried and solid. My guess would be that, depending upon how the spray-drying was carried out, it would have a considerable bearing. In spray-drying you are operating at reduced temperatures, and therefore one would expect a more desirable product, and in my own experience that has generally been the case. However, if that spray-drying is carried out at too high temperatures and under insufficient vacuum, it is conceivable that with the greater surface exposed one might get polymerization or something of that nature. That part of it would depend on how the material is prepared. The other disadvantage of spray-drying is the somewhat greater difficulty in dissolving. The material tends to float on top and is difficult to agitate back into solution.

Chairman Wagoner: We have tried both the solid and the spray-dried type of extract, and we never could detect much difference in the results on the leather.

Mr. Jones: I would say that the same also applies to us in the case of sheepskin leathers.

With regard to the question of dissolving, the fact that in the case of drum tanning the material can be added dry has been one of the good reasons for considering it. It is not predissolved, and we have no difficulties. As far as lightfastness is concerned, we have not seen any improvement at all.

F. A. Coombs (Howe & Co. Pty. Ltd., Melbourne, Australia): It might be of interest to the members here to just have a brief résumé of the type of tannage that has been used considerably in Australia for the production of

upholstery leather with full vegetable tannage. Some of the points relating to the methods do have a bearing on what has just been discussed.

The method used almost entirely now is drum tannage on top of a pickle, with sufficient pickling to yield a uniform pH, preferably between 3.6 and 4. Salt concentration is in the vicinity of 7% in the liquor. The amount of extract used is in the vicinity of 30% of solid extract on the white weight. The extract is mimosa in the main, with about 60% to 62% tannin. The time of tannage does vary considerably depending upon whether it is just a straight pickling after deliming and bating, and the tannage in the drum being straight on top of the pickle.

In some instances they may have a prior tannage in the paddle using the spent liquor from the previous pack tanned in the drum and adjusted to a suitable pH.

This time of tannage, on top of the pickle liquor in drums with temperatures working up to somewhere in the vicinity of 35° to 40° C. as final temperatures, is usually approximately 4 to 5 hr. That is on leather that would have a split weight of approximately 1.5 to 2.0 mm., which would be in the vicinity of approximately 3½ to 5 oz., I think.

With regard to the addition of extract, both liquid and solid (not powdered), extracts have been used consistently with good results, breaking up the solid mimosa extract into small lumps and tossing it in solid, and in no instances have I seen any trouble with that particular method.

MR. LAUDER: What was the rpm of those drums?

MR. COOMBS: The rpm varies quite a bit on the drums. I have used this method for upholstery tannage in two different tanneries. In one we used an rpm of approximately 12, and in the other it was around 4 or 5, the time of tannage in the latter being considerably longer than the 4 to 5 hr. obtained in the earlier case. There is generally a fair amount of drawing and pebbling of the grain, but it has been found that to a large extent that can be eliminated by attention to setting out and wet straining after fatliquoring. We have in some instances resorted to pasting, with excellent results.

MR. PRESLEY: The drum tanning that you mentioned is getting to be the popular way of making upholstery leather at the present time. The rocker yards are much slower, and a softer, more drapey and mellow leather such as you obtain from the drum tannage is more in demand at the present time. People are getting away from flat leathers. There is a tendency in your drum tannage for the leather to be soft, and if you paste after fatliquoring, you seem to firm up the leather a little bit. Milling and softening during the finishing steps produce soft leather again. Drum tannage has other assets in meeting finish requirements. For some reason or other, for the lightfast-

ness properties which the automotive people demand, that is the only tannage to use.

MR. COOMBS: We have mainly been supplying to the automotive trade, and a drum tannage was used in the first instance to try to produce a more mellow type of leather and to reduce the amount of stock in process during the time required to complete the tannage. It was developed entirely to overcome that and to produce a mellowness that was desirable.

We found that as far as the color of the tannage was concerned, the pH and salt concentrations in the final pickle were of prime importance. Wandering away from the figures I mentioned produced a firmer type of leather with more redness in it, and we had to keep fairly close to those figures in order to obtain a nice straw-colored leather with a feel that was as soft and mellow as desired.

With regard to the firming-up after pasting, that depends on the drying conditions in the pasting unit. But we have been able, without any stringent softening action, to produce the softness that is required.

The resultant leather has been used over the past ten years to my knowledge in the automotive trade in Australia. One factor, of course, that we do find is that there is a tendency (unless you are particularly careful) to get some looseness in the flanks, depending on what type of hide you have. But that leather has been used satisfactorily in the automotive industry and in the furniture trade in Australia for many years now.

CARL G. TELANDER (Raser Tanning Co.): I would like to ask the gentleman from Australia to discuss a little bit his oiling processes.

MR. COOMBS: Possibly it may be better if I give a full description of the process as we have used it. We split in the lime, retaining the split condition. The main reason for splitting in lime, in our case, was that it allowed us to convert into whatever type of tannage we liked without being left with all vegetable-tanned splits, and carried on through to a shaving after tannage. Fatliquoring is carried out in the drum with about 7% total oil, using a mixture of 5% sulfonated oil and 2% free oil, such as neatsfoot, cod, or whale oil. From the drum the hides are horsed, set out, and then pasted or strained on toggle frames. The dried leather is buffed, softened, and finished.

CHAIRMAN WAGONER: We have had several allusions to the effect of neutral salts on vegetable tanning. Allen, would you want to say something on this subject?

MR. LAUDER: One of the effects of neutral salts in the tanning of vegetable leathers is to slow down the tannage to some degree. Neutral salts, of

course, are part of the nontannins. The nontannins in the tail liquors penetrate ahead of the tannin and in this way prevent casehardening. This is also one of the properties of the neutral salts.

DR. ROBERT M. LOLLAR (Armour Leather Co.): I have a question for Dick Jones on the tanning of sheepskins for lining leather and the problem of getting full flanks from the lighter-weight skins: Would you care to comment on the proper selection of extracts and syntans and materials that can be used in vegetable tannage in this regard?

MR. JONES: This of course has been one way to take care of extremely lightweight rawstock, traditionally. Today, however, we do not find this quite as much of a problem. We either have heavier-weight rawstock and purchase same, or we can put what lightweight rawstock we have into other end uses. Specifically in answer to your question, however, we have always found that quebracho should be the main constituent of the blend and that it will impart the greatest degree of fullness, filling of the flanks, etc. The mellowness of the resulting leather is usually altered by the addition of wattle or syntans such as Orotan TV. I would say that quebracho without a doubt should be the main constituent of the blend for a maximum in filling and firming properties of the leather.

MR. KAY: Would you modify your bisulfiting?

MR. JONES: That is another approach. By and large we have always used a bisulfited quebracho in the neighborhood of from 4% to 6%. It is not usually necessary to use a less bisulfited quebracho to obtain more firming characteristics.

MR. KAY: You have not found that the lesser amount of bisulfite produces a fuller and firmer leather?

MR. JONES: Yes, but we generally have no need of going in that direction. We would prefer starting with about 4% to 6% bisulfited quebracho, which will give us the maximum we want in filling and firming. In fact, we often have to alter and go in the other direction in order to get more mellowness by the addition of other tans or syntans.

MR. KAY: Actually, part of the problem, I think, comes from the beamhouse. If you overdisperse the fibers in the bating and in the previous processes, you accentuate the problem in the end. You can switch bate from chloride to sulfate bate and improve the skins from that standpoint, and then your tannage combines more uniformly in the direction you are thinking of.

DR. LOLLAR: Here we are talking of the situation where the skins are from New Zealand, and where we have no control over that factor and therefore have to live with what we have.

MR. KAY: Quite true.

MR. LAUDER: The blend you have mentioned would not be the same as has been reported for bag, case, and strap leather. Quebracho would be the main part of the blend. Wattle would come up close to it. You cannot use too much chestnut, or you will get your leathers too firm. And certainly you will want to keep valonia and myrobalans to a minimum, or they will affect the color. They will also tend to give you some sludge in the tan yard. If your quebracho is slightly bisulfited, you are going to have more insolubles, and as a result you are going to have more sludge. I am not sure that this is economical.

ROBERT G. WELDON (Radel Leather Manufacturing Co.): In the manufacturing and processing of sole leather, are you making better sole leather now that you are starting to pretan with chrome or putting synthetic in your tanning material before you use your vegetable tannage? Does that make it a better piece of sole leather?

CHAIRMAN WAGONER: Are you referring to the combination type of tanning?

MR. WELDON: Yes. Mr. Kay mentioned pretanning with chrome, on sole leather. Does that make it a better piece of sole leather—this new process?

MR. LAUDER: Better for what?

MR. WELDON: Wear, plus all the physical characteristics in a piece of leather.

CHAIRMAN WAGONER: From the wear standpoint, the combination of chrome and vegetable has been quite well known. It gives an improved wear characteristic. Of course wear is only one factor in sole leather, and the combination tannages have created some problems in shoe manufacturing. But I believe these have been largely overcome. Strictly from the wear standpoint, however, I think it would be an improvement.

OSCAR V. WEDERBRAND (Rohm & Haas Co.): I have this question for the panel as a whole. Going back to drum tannage versus pit tanning, it seems to be at least my interpretation of what the panel has said, that the con-

sensus is that pit tanning produces firm leather and that drum tanning produces mellow leather. Is it possible to produce the same kind of mellow leather in pit tanning? Or do you have to go to drum tanning in order to get mellowness?

MR. KAY: I think it all depends on conditions, Oscar. If you want to make a mellow leather, you keep your acidity down, and pH and salts up. The advantage of the drum tannage is that tannage is taking place with the fibers flexing. You have less danger of the tannin combining on the surface of the fibers, with a form of incipient casehardening. At least that is the way I think of it. In drum tannage the fibers are constantly flexing, and the tannin has a better chance of getting in, and it is constantly softening the fibers, so that the fibers cannot recoalesce; and therefore you get a better distribution of the tannin into the fiber.

You can achieve the same thing by pit tanning, of course, but drum tannage is more convenient. With drum tannage, if you want to get firm leather, you have to work hard to get it. With pit tannage you have to work hard to get soft leather.

MR. LAUDER: Not if you first leach. There are very few leachhouses left in America, but with leaching, you can certainly get a more mellow leather in pit tannage than you can without it. You are recirculating some of the liquors, and as a result it appears you do get a more mellow leather.

CHAIRMAN WAGONER: Would that be a case of using lower-strength liquors?

MR. LAUDER: No, I would not say so. Of course it depends on what you are concerned about. If you are talking about sole leather, you will use a higher-strength liquor than in bag, case, and strap leather. But it would not mean that you are using any lower-strength liquor in bag, case, and strap leather than any other similar manufacturer would be doing without leaching. And the manufacturer who leaches first, I would say, would get a mellower leather.

MR. KAY: Actually, when you leach you have a less pure liquor. Certainly the organic nontans would behave similarly to neutral salts. Again, you are getting more thorough penetration from a leach liquor than from an extract—would you say that?

MR. LAUDER: I would say that, yes.

DR. H. G. TURLEY (Rohm & Haas Co.): There is no question about the fact that these two types of tannages produce fundamentally different

leather. In pit tannage the fibers are in a full condition and with low salt concentration. In the drum tannage, on the other hand, you are starting with pickled skins. The fibers are depressed and unswollen; the high percentage of salts produces osmotic effects and produces a different result. It is possible to make firmer leather in the drum and a more soft and mellow leather in the pit. This has been done in Morocco for many hundreds of years. They make goatskin leathers using vegetable tans.

We have to give more attention to the fact that we are dealing with two fundamentally different ways of tanning here. As far as I can see, you can make two kinds of leather, independent of the equipment, as long as you take into account the basic factors.

MR. JONES: That is an excellent point, Dr. Turley. I wonder if anyone in the audience has had any experience in the case of drum tanning with varying the salt concentration, and its resulting effects?

JACK H. TRAUB (J. A. Lang & Sons Ltd.): There is a material of Australian origin which uses the name Myrtan that has been on the market here and in Canada, too. I wonder to what extent you have been able, in Australia, to take advantage of that material in your tanning?

CHAIRMAN WAGONER: Is it eucalyptus wood extract?

MR. TRAUB: Yes, under the name of Myrtan. Is it common in Australia?

MR. COOMBS: Myrtan has been used in Australia, but it is not from just one type of eucalyptus. It is from various types of eucalyptus and has been marketed for years. The use in Australia of Myrtan might not even be as common as in other parts of the world.

The wattle extract and the mimosa extract, not as extracts but as tanning materials, were indigenous to Australia. As everyone knows, wattle extract is available in quantity from South Africa, but South Africans obtained the wattle trees from Australia in the first instance.

Myrtan has been used mainly in a blend with mimosa extract. It has been used in soft leather tanning in Australia to a small extent. I have used it, myself, as a percentage in blends, in the chrome-retan leather for uppers. The properties of the Myrtan extract are somewhat astringent—thinking of the straight Myrtan. And Solex is less astringent. But the general properties are a firmer quality of leather. The sole leather people when they first tried it out found that the penetration was, as you would expect, quite slow by comparison with mimosa. It has been used on occasions in chrome-retan leather, and I have found it quite useful when I wanted to tighten the grain and obtain some firmness without altering the over-all process from the beamhouse on.

MR. JONES: Would you care to comment on its solubility and color?

MR. COOMBS: Quite frankly, I have not used it to any great extent. The color is generally somewhat darker. I have not had any great experience with its solubility, that is, compared with other extracts. But I have not actually heard of any difficulty in solubilizing the extract.

As I mentioned before, to a large extent I have found in tanneries that I have been associated with that the use of solid extracts is quite satisfactory, and I have not gone to the extent of solubilizing and forming liquors with a lot of the extracts that I have used over the last 15 or 20 years.

MALCOLM H. BATTLES (A. C. Lawrence Leather Co.): It is interesting that the common way of describing bisulfited extracts is 2%, 4%, and 6% bisulfite. It has been demonstrated that this is not necessarily indicative of the product produced, although most people in describing them still talk of them this way. It is entirely dependent on the conditions of bisulfiting as to the final product produced.

I would like to direct a general question to the panel as to what analytical procedures are used generally today to further classify these extracts chemically.

CHAIRMAN WAGONER: There has of course been quite a bit of work done on analysis of bisulfited extracts, by Dr. Turley and his group, a few years back. In general practice we do not break down the analysis to that extent. We usually measure the amount of solubilization of it.

You refer to the manner of bisulfiting. One of the things, of course, that can vary the resulting extract considerably is the construction of the tank—whether you have a high, narrow tank or a low, quite wide tank. That has a considerable bearing on the insolubles—the depth of your extract during the time of the bisulfiting period. Also the treating time and temperature. But we do not, as a general practice, make an analysis of the type you have reference to now.

MR. BATTLES: I can understand why, after conducting a few. You have an indication of this by your sedimentation, which is the point I wanted someone to bring out. When we are talking about a bisulfited extract, we should be careful not to classify all 2% bisulfites as being alike, because they are not.

MR. LAUDER: However, is it not wise to have a standard to which you are bisulfiting? In other words, suppose you want 0.5% insolubles, is it not wise to analyze now and then to find out how close or how far away you are from that standard?

MR. BATTLES: By analyzing, you mean chemical analysis?

MR. LAUDER: Yes.

MR. BATTLES: Yes, it certainly is. But to take the 0.5% insolubles here, the figure you mentioned—how do you determine this?

MR. LAUDER: By the standard ALCA method.

MR. BATTLES: Which is not a chemical analysis for degree of bisulfiting. It is again your qualitative indication.

MR. LAUDER: That is true, but does it not tell you the percentage of insolubles that you have?

MR. BATTLES: Yes, I agree, you have a standard. But how does the percent of insolubles relate to the way it has been bisulfited?

MR. LAUDER: I think it does, because if you don't bisulfite correctly, your insolubles will increase. It does not necessarily tell you the percentage of bisulfiting, but it does give you some idea of how thoroughly your bisulfiting job has been done.

CHAIRMAN WAGONER: In that sense it would be used purely as a control measure for batch-wise checking, and as you point out, it would give you an indication of whether you are doing a good job of bisulfiting as measured by the reduction in the insolubles. But it does not, of course, with empirical methods such as we have for tannin analysis give us the amount of SO_2 that might be left in the liquor or extract, or the different results on the tannins themselves. So that the insolubles determination is purely a control type of test.

MR. KAY: I wonder if the question is not intended to be a little deeper than has appeared on the surface. What are we looking for in our analysis, and what does analysis mean? This I think is a fundamental point in all of our discussions. If you read the official methods of analysis, they clearly state—I don't remember the paragraph number right now—that it is merely a method of obtaining a basis for agreement between buyer and seller—period. It does not tell us what is happening in the tannery liquors as used. That I think is a problem and a real problem.

My own approach has been—and Mr. Battles hinted at it, and I think he does the same thing—to develop our own methods to try to determine just what is taking place in the tannery, where we are going to use it. What the

analysis is and what we find by official methods is one thing. But how we use it is the important thing.

My own method has been to set up a sedimentation-type test. We take the bisulfited extract and dilute to about 20 barkometer, which we find seems to give a maximum figure for insoluble matter. We then centrifuge that. We take the total solids before centrifuging and the nonsettleable solids afterwards, and the difference we call the insolubles. You can argue with that premise, but that gives us a reproducible figure. We then calculate it to 50% solids. The pH is normally adjusted to 4. If we want to use it for scrubhouse work and have to have scrubhouse liquor at pH 3, then we run it at pH 3. That, I think, tells us a great deal more about the leathermaking properties of the material than any chemical analysis, *per se*. Would you agree with that?

MR. BATTLES: Yes.

MR. KAY: I think it is a very important point. People use liquors with 2% to 4% bisulfite and also worry about sludge in the liquors. You can have two liquors with 4% bisulfite, which is the optimum for solubilization within normal pH limits, if properly conducted at the proper temperature for the proper time, which show the same official insolubles. However, when you come to use those, one extract at normally 4% will give you a lot of sludge, and the result is stained and blotchy leather; the other will give you a nice clean liquor, with no sludge, and also clean leather.

So, personally I don't think that "chemical" is quite the word we want. Perhaps "physical" is a better description.

DR. TURLEY: Might I suggest something? I do think we need a chemical examination and to go further along the line, as we did in our laboratory when we opened up the analysis of bisulfited extracts some years ago. We got an insight into what was happening in bisulfiting. This method that we worked out I was told was of great value to the United States Leather Company—I think I can mention this now—because it was the basis of checking three independent means of bisulfiting. Although they were supposed to have had the same process, they came out with different liquors. It is very intriguing that you can get different chemical products by the degree to which the bisulfiting action penetrates. You go from the early stage of solubilizing and get the sulfite loosely attached—sulfite esters, so-called, and you go through to the hydroxy and even nuclear sulfonic acids.

I call to your attention that those products have very interesting and different qualities. The more intense the penetration of the sulfonic group with quebracho, the more firmly fixed are the tanning agents.

We had a man from Australia who was indebted to us. He was buying an expensive bleaching extract. Now in some types of tanning they use "bleaching extracts". We found that essentially the bleaching extract was lightly bisulfited, but containing an excess of sodium sulfite. So he was able to sulfite and add in his own bisulfite, thus saving considerable money.

You will find, I think, from looking at all the work, that if you take *X* % as your figure for bisulfiting, as you study the temperature and time you get changes in the composition and you could make a half dozen different extracts, all of them with 6% bisulfiting.

MR. KAY: You are exactly right, Dr. Turley. I should have clarified the point by saying that I was limiting my remarks essentially to yard extracts.

When you come to the scrubhouse extract, where you are not using it for actual tannage, *per se*, you definitely want a better-dispersing type of extract, something more closely approaching a syntan. Very definitely it has a considerable bearing. But it comes back again to what I said initially. One has to develop tests, and utilize such tests, to tell you what you want to know. And what you want to know at any particular time, of course, depends on what you are trying to determine.

MR. LAUDER: The method of bisulfiting is important. At no particular time should the temperature go lower than 170° F. And if you have a good foaming action at the point where it is almost ready to flow over the top of the boiling tank, you are controlling the boiling at the best point. It is important that a man be there at all times and that it be carefully controlled.

MR. KAY: I would go further than that and say that at 170° F. you will not get bisulfiting that is worth speaking about. In my opinion you have to operate at close to 205° F., at least, to get solubilizing within a reasonable period of time.

MR. LAUDER: I will agree with that 100%, but when you are adding your bisulfite—your dissolved bisulfite—your temperature sometimes can take a fast dip, and it is important that it not go below 170° F. at that point.

MR. PRESLEY: On this 2, 4, and 6% bisulfiting, these figures can be rather ambiguous. A lot depends on the bisulfiting practice, itself. As Jack mentioned, a 2% bisulfiting in a large-diameter tank can be far different from that in a narrow, high tank. You have both your temperature variable and the speed at which you add the bisulfite. In other words, there is the contact of the bisulfite with the liquor that has a big bearing on the end result. When treating an extract in a narrow, tall tank, the bisulfite will certainly be in contact much longer then when you have just a low tank. Also, the method

of agitation, whether you use a paddle or whether you use air or steam, will make a big difference.

I think rate of addition and method of agitation are probably the two biggest variables in bisulfiting any extract.

CHAIRMAN WAGONER: In this matter of sludge formation that we have touched upon, I might describe briefly a series of tests which we carried out a few years ago. In order to determine what was happening to the insolubles as well as the tannins, we drew samples through the course of the blending operation for analysis. That is, a sample was taken of each of the original extracts. At that time there were five or six. The quebracho was sampled after bisulfiting, and samples were then taken after the addition of each of the other materials, such as wattle, cutch, myrobalan, etc. These samples were then analyzed by our Official Tannin Analysis Method. It was interesting to find that with the addition of the various extracts we actually got a conversion of tannins to nontannins in some cases, and then again it would reverse itself and we would get a conversion of nontannins to tannins. Likewise, we found that the insolubles increased or decreased during the blending procedure. These batches of extracts were then followed into the liquor preparation, and here is where we found the largest formation of insolubles, which, of course, can be attributed to the effect of dilution. Using this approach we have convinced ourselves, at least, that a good deal can be done in reducing the insolubles in the liquors, if the blending is carried out under properly controlled conditions. We strongly advocate the use of temperature controls on all the blending operations and sticking to the temperatures which we have found to be most effective in extract handling.

I know we had one case in particular where one of our tanneries was noted for the amount of sludge in its liquors. When we studied its procedure of blending extracts and established one that we thought was the best as to order and temperatures, we were able to reduce immensely the amount of insolubles being formed. Of course it took a few months to work through the sections.

LESTER M. WHITMORE (Leas & McVitty, Inc.): We bisulfite at 4½%, and we do as Arthur does—dilute the sample. But we merely cook until we get a clear solution at 10° barkometer. We find that 4½–5% is all that is necessary to get good bisulfiting on practically all extracts, if they are cooked long enough.

But in any plant procedure, time is a factor. It takes longer to heat it up in the winter. We add some bisulfite with the extract and the rest of it later. Twenty-four to 36 hours usually does the job.

I understand some people vary the amount of bisulfite with the amount of insolubles in the original quebracho, which may be theoretically correct, but

we find that 4½–5% is usually sufficient. We practically never have to add any more in order to get a clear solution.

MR. KAY: We have done some work on that, going back to the original extract. Running a sedimentation test is what it amounts to, on the raw materials. The different brands of quebracho vary in the raw. They also vary from shipment to shipment. However, what we find is that, on bisulfiting, the sedimentation insolubles seem to be independent of what we find on the raw extract, either by ALCA or sedimentation. There seems to be no connection between the two. We also find, however, that there is a considerable difference in the sedimentation insolubles of different brands after bisulfiting. And that seems to hold quite consistently. Some brands give us consistently low results and other brands give us consistently high results, and that seems to be borne out by our tannery practice.

MR. WHITMORE: Does that tie in with the insolubles in the original extract?

MR. KAY: Not too well. We now evaluate samples in a small way in the laboratory, and after bisulfiting, we inspect the sedimentation figure. It is that figure which seems to be significant as far as actual tannery use is concerned. What the extract had in the raw does not seem to be too significant. You may have one that has 8% as measured and another that has 10%. After bisulfiting, the 10% extract may give you lower insolubles than the 8%.

CHAIRMAN WAGONER: We have found that, too—not on laboratory-scale tests but checking through plant batches—with several different brands of extract showing different amounts of insolubles by original analysis. We were able to account for practically all the insolubles, and it did not matter whether they had a 6 or 8% insoluble content. We used 4% bisulfite on the weight of the extract in all cases, but we could not detect any difference. It still came out as analyzable tannin, practically all accounted for.

S. DAHL (National Bureau of Standards): Several years ago there was a committee formed for the determination of lignosulfonates in such blends as you are talking about. I am wondering if anybody can tell whether there still is any great demand for such work.

MR. KAY: The determination of lignosulfonates?

MR. DAHL: Yes, in blends.

MR. KAY: You and I have argued fiercely on that subject. Personally, I think we have a method that is sufficiently precise. I think the cinchonine

method, with proper controls, gives good results. We have made checks with manufacturers of lignosulfonates on blends they have submitted—they did not tell us how much was in them—and we checked out rather closely.

CHAIRMAN WAGONER: The cinchonine method?

MR. KAY: Yes.

MR. LAUDER: Some mention could be made of purity—the control of purity in the yard at a particular time, and what purity is. Purity is the relationship between tannins and nontannins in an extract or a liquor. Tannins plus nontannins equal soluble solids. And the percent tannin over the percent soluble solids times 100 equals the percent of purity.

In bag, case, and strap leather tanning, the purity of the head vat liquor should be in the range of 65 to 75%, and the tail vat liquor in the range of 30 to 40%. If the barkometer on the tail vat liquors remains constant and the purity drops below 30%, this is an indication that nontannins have increased and tannins have decreased. This of course will slow up the rate of tanning. If the purity of the tail liquors rises above 40%, then tannins have increased over nontannins, and there is a possible danger of slight case-hardening which will help to slow up diffusion of tans into the center of the hides.

I mentioned the tail liquors as an example. If the counterflow system is not closely controlled, impurities may rise or fall throughout the system. If this occurs at the head end of the system, it may be corrected by regulating the flow of fresh liquors to the head vat. If it occurs at the tail end, it may be controlled by regulating the amount of sewering of the tail liquors.

CHAIRMAN WAGONER: This problem of purity, of course, has changed quite a bit with the increased use of extracts. I think pretty nearly everybody has been forced to use higher-purity liquors. Allen talked about 40%-purity liquor in the tail liquor. I remember not too many years ago that if a tanner had 40%-purity liquor in the tail liquor he really would be alarmed. So we have had to change our thinking and our operations in relation to the purity of liquor; the density of the liquors, of course, has to be taken into account too.

MR. LAUDER: Perhaps some of you still do use lower purities. If so it would be interesting to hear about it.

CHAIRMAN WAGONER: There has been mention a few times about the leaching of materials versus the use of extracts today. One phase that has been discussed quite a bit is whether it is cheaper to leach or to handle the

extracts. I wonder if anybody has anything to add in that category. We had occasion to look at it a number of years ago, when we went off leaching, but I never felt that our leaching operations were big enough to give a fair comparison.

MR. WHITMORE: We continue to operate leachhouses, and we have evaporators in each tannery. It is really a small extract operation and enables us to concentrate the liquors. From a labor standpoint, in addition to handling the material, we have to have somebody there, even if just for mixing. And our evaporator operator attends to the mixing. Whether we would build a leachhouse under present conditions, I don't know. If you already have one, that is one thing, but if you had to build one, it could be quite an expensive job.

FRANK J. CHADWICK (Crystal Extract and Chemical Company): May we return for a moment to the comments made about Myrtan, the eucalyptus wood extract? The gentleman from Australia commented about eucalyptus extract being made from a variety of species of the wood. That is not the case today. Eucalyptus wood extract was brought into being in 1937. That is relatively new by the standards of other wood extracts. Therefore, there were going to be a number of problems that the producers faced in developing the material that would be desirable for tanning purposes. But today eucalyptus wood is extracted from one species—the *Eucalyptus redunca.* It is grown only in Western Australia. As I look around the room here, I see quite a number of tanners who use substantial quantities of the Myrtan extract with very desirable results. I just wanted to clear up that point.

MR. COOMBS: I am very sorry if I have given any wrong impression in regard to Myrtan. I thought I had indicated in my remarks previously that I have not been a great user of Myrtan. To a large extent my information has been obtained from personal visits of the Myrtan extract people in Australia, and I may have made an erroneous statement in saying that it was made from a blend.

I would like at this stage to correct any impression that it is not a material that can be used to distinct advantage in tanning. I have not been associated with sole leather tanners since 1947. In and around Sydney, Australia, where I have been, and in Melbourne, we have been manufacturing light leathers, and you can well imagine that the type of extracts used in our case is different.

With regard to the use of extract in the light leathers, I have seen light leathers made from the sulfited eucalyptus extract. The *Eucalyptus redunca* is one of the prime species used in Australia for the manufacture of the eucalyptus extract, and I want to withdraw any remarks that may have been misleading in any way.

DR. LUDWIG SELIGSBERGER (Quartermaster Research and Engineering Center): Some years ago one of the conventions in Germany was startled by the announcement of an Argentine process which was a dry tannage with sulfited quebracho and chrome pretannage (*Leder*, **9**, 163 [1958]; **10**, 12 [1959]. I wonder if this process has ever been demonstrated in the United States. As I remember, there was no liquor left after the tannage. Of course, it was not up to standard in color. I wonder how such a process compares with the drum tannages which were mentioned, where I presume the sludge is rather large.

CHAIRMAN WAGONER: I think I know the process to which you refer, but I have had no experience with it and don't know whether anybody has tried it out in this country.

GEORGE A. STEVENS: With regard to vegetable and mineral tannage, is there anything that you can get with vegetable tannage that you cannot get with mineral tannage? In other words, chrome- and vegetable-retanned compared with straight vegetable?

MR. LAUDER: I would like to answer in part. Other members of the panel may carry on, because every leather has different properties.

Vegetable tanning produces leathers that have less stretch than mineral leathers. For this reason vegetable leathers will hold a print better after embossing, when the leather is stretched. Vegetable leathers will wet back faster and swell more readily and therefore are useful for the manufacture of mechanical leathers. They can be beautifully tooled and carved. I have stood in awe at the beautiful artistry of the Last Supper carved in a panel of vegetable leather. Vegetable leather, in itself, has beauty. It requires no plastic finishing to give it fashion. A retanned leather, or a semistuffed, or stuffed and finished leather in the russet, which is the natural tan, can make fine luggage, purses, and wallets. Such leather has even been used to enhance the walls of a superhotel, where it creates a western atmosphere. If Harry Berndt is here, I wonder if he will say something about that.

HARRY C. BERNDT (The Lackawanna Leather Company of Canada): It is true that I used vegetable leather, which we bought from a Canadian tanner. We did two tremendous walls in large pieces of strap leather, and they lent themselves to beautiful tooling and decoration. I do not believe that we could have done it on anything except that leather. We did not apply a color coat to the leather. As it ages it becomes more beautiful from the natural darkening and reddening of the leather itself.

MR. LAUDER: Were there not brands on some of that leather?

MR. BERNDT: Yes, 340 different brands in one room, done by carving.

MR. LAUDER: I think I may mention where that room is. It is the Alberta Room of the Royal York Hotel in Toronto, in a new wing. Also, is there not a large mural in leather in the Shell Building in Toronto?

MR. BERNDT: Yes.

DR. TURLEY: Mr. Lauder, I agree not 100% but rather 1000% with what you have to say about vegetable leather. Vegetable leather is not only a tradition, but it is also a beautiful product. It has a quality of warmth and character which is outstanding. The mineral leathers cannot compare. But, in spite of all we can say, there is less and less vegetable leather. Where we used to import 125,000 tons of quebracho, imports have dropped down to 50,000 tons now, I believe.

Can we have a discussion on ideas for an attempt to improve vegetable leather and get it back in popularity? We are faced with some potential competition from outside sources. I refer to the plastic materials. We must do something about that. Otherwise, we will be talking about a very small quantity of a very beautiful product.

CHAIRMAN WAGONER: That is certainly a good subject because it is one that I know has been given a lot of consideration by all of us—that is, how we can enhance the use of vegetable-tanned leather. From a technical standpoint, we have to consider new applications, new ways of using it, and new uses for that type of leather.

Of course we would like to see more of this panel-type decoration with it. That is one of the outlets that has been pushed for its use. And in shoe manufacturing, of course, we have to agree 100% with Dr. Turley that the esthetic value of good vegetable-tanned leather is certainly a big thing. But when we get into the market place, we are forced to consider the dollars and cents. Therefore, we have to try to devise means of producing our leathers at a cost which will permit sale at a profit. That seems to be a foreign word in the leather industry today.

I think a good deal of work has been done and is being done toward that end. A good many of our discussions here on the advantages of drum tanning versus pit tanning are directed toward achieving our end product through a reduction in time and, if possible, through a reduction in costs.

MR. PRESLEY: This will probably have some bearing on the last two questions. In the case of vegetable-tanned leather where we use a straight vegetable tan such as in the rocker sections, we get fairly firm leather. After retannage we used to use a high amount of fatliquor to lubricate and obtain the

desired softness and mellowness. Then we started running into trouble with specifications of the automotive industry. The high fat content in the vegetable tannage caused trouble with the yellowing test. Now, to offset that you use the so-called rapid drum method, chrome tan and then a light vegetable retan. You also use less oil. You can use oils along the sperm and neatsfoot line rather than cod, all to improve the yellowing tests.

Referring to the figures that Dr. Turley mentioned indicating how much less quebracho we are using—maybe we are using less, but our production of upholstery leathers is still only slightly reduced from what it has been, although it is true that the economics of so-called imitation leathers is cutting into the production of our upholstery leather.

E. R. LOBAUGH (Saxe Cutch Corp.): Speaking of the reduction of imports of vegetable tannins, as Dr. Turley mentioned, one of the things we need to learn is how to use our research. We have talked for years and years of the value of research, yet we hear research discussed with negative results. We just don't know how to use our research apparently, and that is one of the answers to Dr. Turley's question and comment.

MR. WELDON: The use of vegetable leather, according to the Tanners' Council statistics, is down 60% in the last 5 years. I just wanted to clarify the question that you raised, Mr. Presley.

In regard to the other question, Mr. Lauder said that chrome leather stretches, and this and that. We are not going to debate as to the fine qualities of one type of leather or the other. I just believe that chrome leather can be made so that it does not stretch and so that it has certain beauty; I believe also that vegetable leather can be made to have very beautiful qualities. But let us not say that one is this and the other is that, when it is just a matter of opinion.

MR. LAUDER: Not once did I criticize chrome leather. That was not my intention.

MR. WELDON: You said it was stretchy.

MR. LAUDER: But believe me, I am on fire as far as this business of merchandising leather is concerned. Because in so many instances we are losing out. You can talk about the economic end of it if you like, but we must not only put life into our leathers but also life into the leather industry. If we don't do it, then I will say that this symposium has been held in vain.

I would like to go a little further. I am not attempting to compare one leather with another, but stating the qualities of vegetable leather. In the russet state it can give fashion to luggage, to wallets, to handbags, and so

forth. Vegetable leather assists in bringing electrical power and communications into your home and factory. It protects the lives of hydroelectric and telephone linemen, as they use sturdy, long-wearing safety belts. Vegetable leather in its russet state continually suggests to people the original leather look. When they look at it they know it is 100% leather, and not plastic. I feel that it is important in the manufacture of bag, case, and strap leathers that the russet leather-look should be perpetuated, as this is a tanner's finest propaganda, and this leather is most difficult to simulate.

ANDREW SALAMATOV (Barrett and Company, Inc.): It has been said that vegetable leather is beautiful. There is no question but that vegetable leather has its merits. But in connection with this, I would be interested to find out why it is that it has almost completely, or at least practically, lost its market in the shoe manufacturing industry. Can we sweep everything under the rug in the name of economics, or is there anything inherent in the intricacies of the interaction of unknown vegetable tans with the unknown collagen fibers that could be clarified? Take the problem of scuffing, for example—grain scuffing. Has anything been done by the vegetable leather manufacturers to improve that quality?

MR. KAY: You have a good statement there. I wonder if the shoe manufacturers can tell us why vegetable-tanned leather is used so little in shoe uppers? That might give us some indication of what to do in order to bring it back.

MR. CHADWICK: There is a channel of marketing of leather to the shoe manufacturer. I happen to work in the Midwest area where there are quite a few manufacturers, in the Milwaukee District, who come in contact with the shoemakers. A man goes into a shoe manufacturer with a line of leather. He is an agent. He not only has a line of leather, but he also has a line of synthetics—synthetic welting, synthetic innersoles, and other items.

Perhaps the manufacturer will give him a substantial order for leather heels, and he is then satisfied with that order and does not fight for the upper leather business or for the sole leather business, if he happens to be handling a line of soles. I think we should look to the marketing of our leather directly from the tannery rather than through agents.

MR. KAY: That is hardly our responsibility.

DR. PETER R. BUECHLER (Rohm & Haas Co.): I would like to echo Mr. Chadwick's comments, to this extent: A lot of the problems in the leather industry are due to the fact that we are not merchandising correctly. Insofar as finding new markets is concerned, the sales departments of the leather firms are very remiss in this respect. I can cite one interesting example of this.

Several years back I was working for a corporation which was subsidized by six tanning companies. During that time I was contacted by a man from the Minnesota Mining and Manufacturing Company who became very interested in the possibilities of using leather on the rolls of printing presses under a bead-type of material. The requirements as to thickness were quite high. You had to split very carefully, but it was within the possibilities of a good splitting machine and a good splitting machine operator. The leather pieces were to be 4′ x 3′, and they were to be sold in large quantity, if they were successful. One newspaper alone, I was told, used a thousand such rolls per month. I mentioned this proposal to six companies and told them that Minnesota Mining and Manufacturing would do the research if we would send them some leathers. Each of the technical people to whom I addressed my comments decided that he should refer the matter to his sales department. Some two months later I contacted Minnesota Mining and Manufacturing Company, and not one thing had been done by any of these companies, or by their sales departments at least, in exploring this possibility of a new leather use.

I would like to suggest, now that we are getting (through A.S.T.M.) some of the procedures and physical characteristics for our leathers quite well defined, that we should employ through the Tanners' Council or some other such group a market survey group to explore the possibilities in fields other than where leather is now currently employed. We don't want to have just a bunch of order-takers calling on the same old shoe companies or other conventional outlets. Let us look to new places.

CHAIRMAN WAGONER: That certainly points up a good thing. I am wondering, and I have wondered, what we in the technical group can do toward merchandising leather. Have we been remiss in translating our findings, as far as the properties of leather are concerned, properly to our sales promotion people? Do we furnish them with the type of information that is needed? Do we know enough about how our leather is used after it leaves the tannery? Have we failed to supply our customers with the type of technical knowhow that would be helpful in using our products?

In the case of sole leather, I think it is a well known fact that the synthetic people—while they did a good promotion job on the fact that their product might outwear leather two to one, and they played it up in advertising—did their best job selling their product in the shoe factories through technical service. They went in and showed them how to adapt it to their machines. I don't think that all of us in the leather business find out enough about what they need to know about handling our leathers. If we can strive to obtain that kind of information and turn it over to our promotional people, I believe that is one phase on which we can do something.

DR. TURLEY: I think the industry has not done a very good job of selling its product on the basic qualities which it possesses. In Europe they are becoming increasingly faced with the same problems. The International Group who will visit us next year in Washington is now giving consideration to a study of the basic quality of leather, in the hope of coming up with certain attributes of leather which other materials do not possess.

One of the big areas of interest is the question of comfort. Dr. Grassman is interested in that problem. Dr. Baum, representing the shoe manufacturers, is interested in the same problem, and there are others. When we can discover some properties that are related to comfort—it has been agreed that leather is a fine product for comfort, and this is important from a physiological and psychological point of view—then we can do a better job with research and manufacturing, work toward increasing these properties, and use them in merchandising our products. No doubt leather has certain positive attributes: it is resistant to water penetration and has vapor permeability. It is also negative in other aspects. The very fact that leather is soft, relatively speaking, now produces problems with regard to abrasion, having to do with luggage, for example, because we are dealing with new methods of transportation. We must therefore get busy and overcome these defects so that leather can have greater abrasion resistance and scuff resistance. We must catalogue the properties of leather, both good ones and negative ones, and work on them accordingly. I don't think we can do much here as far as merchandising is concerned.

MR. KAY: I quite agree, Dr. Turley. I think the people, here, have no control over the merchandising. We are merely centurions. The people who want to maintain the *status quo* will cry "Uncle" one of these days, but until that time comes, I think it is profitless to discuss the things we cannot control.

CHAIRMAN WAGONER: I will have to disagree a bit. I think we do have some control. It is up to us as technical people to provide our sales people with this kind of information. I think that we have been lax, in that we do not participate in the merchandising of leather. We don't even have to go further than our allied trades to get examples of what I am talking about. They have their technical groups as well as their salesmen, who come in and see us and tell us about the technical aspects of their products. I think we have to do the same thing in marketing our products.

MILTON BAILEY (Research and Development Facility, U. S. Navy): Most of the talk here has been directed to vegetable tanning of sole leather. I would like to mention that there is a convincing evaluation history, obtained through wear and laboratory tests, which indicates that combination tannages can give us outstanding wear such as you do not get by using vegetable tanning alone.

This information suggests that there are prospects for both accelerating your process and providing a superior product. I believe the method and material will be valuable to us as consumers and to you as fabricators.

MR. WEDERBRAND: About 25 years ago the Graton-Knight Company in Worcester was producing a sole leather which they called Gold Spot. It was my understanding—my memory, of course, may be faulty—that it was a yard-tanned leather. It was tanned with liquors which were a combination of chrome and vegetable. That leather apparently was the forerunner of the mellow sole leathers which are in demand today, but possibly it was away ahead of its time and, therefore, gradually petered out.

However, along the same lines that Mr. Bailey has just spoken of, is it possible that a combination of that sort would have an advantage? I wonder if any of the panel or others here have put through any tannages of that nature, where the chrome and vegetable are applied to the hide at the same time?

MR. KAY: I have only had some limited experimental experience. A number of years ago I just mixed the chrome and the vegetable together. It was a ghastly looking mess—the liquor as I put it in—but, strangely enough, it made a nice piece of leather. But I have never tried it on a more extensive scale. Was that a cationic chrome, or was it anionic?

MR. WEDERBRAND: I have not the slightest idea. Maybe somebody here has more information about the old Graton-Knight process than I have. I think it was developed by Dr. Small back in those days.

MR. KAY: There is one problem I think we have to face regarding the utility of leather. We have to recognize that the shoe manufacturer does not give a tinker's dam what he puts into or on the shoes. If he could get away with paper, that is what he would use. It seems to me, before we can improve our position, we first have to find out what is wrong with leather from the shoe manufacturer's standpoint and then make something that he can use profitably. Then, somehow, we have to get across to his customers that leather does have these worthwhile properties. It seems to me that we have done neither. We don't advertise, except to ourselves. All of our advertisements are in our trade papers which *we* read. It is nice to know that Armour Leather makes Armatan and that A. C. Lawrence makes Tannage 77. I like to read about it. But I don't think it helps the industry a single bit. I am citing names here only for example, of course.

I think we have a psychological problem as well as a practical problem. What the solution is, I don't know. I don't think the technical man, as such, either has the jurisdiction or the responsibility of solving those problems.

That is something that is strictly the business of management. I think our problem is concerned with the making of leather with properties that are needed, and it is management's job to tell us what properties are needed. We cannot control that.

DR. BUECHLER: I just want to make a comment on this combination of chrome and vegetable tannage in the same liquor. Insofar as I know, the groups which have been concerned with solvent tanning other than the one with which I was associated, have not done this. But we did find that we could put chrome and vegetable into the leather simultaneously in the solvent very nicely and mix the two of them at once, and this solvent tanning system, when it is in more general use, will, I think, be particularly adaptable in that respect.

MR. KAY: Did you find the improved physical properties that were suggested here a few minutes ago?

DR. BUECHLER: We were doing this on an experimental basis and did not manufacture those leathers, but we found it gave a very nice appearance and an excellent grain.

CHAIRMAN WAGONER: Certainly the possibility of the combination-type tannage is one that has been given a good deal of consideration by all the vegetable tanners because we recognize the valuable properties which can be obtained through the use of chrome and numerous other retanning agents. And if we can combine the properties of vegetable with chrome, we can enhance our product in that way. It is one of the things that certainly can be explored further.

MR. JONES: This chrome-vegetable combination has been tried in the past on sheepskin leathers (drum-tanned), and it appears that the amount of chrome should be kept down to something like 0.25 to 0.50% chromic oxide. The main advantage of such leather has been an improvement in the grain-cracking properties.

CHRISTOPHER J. NUGENT (Rohm & Haas Co.): Referring back to Mr. Wederbrand's remarks on Gold Spot, the original Gold Spot sole leather was made with a combination chrome and vegetable procedure, in the yard. I don't believe it was a conventional yard. I think it was more or less a single-vat tannage. In later years that leather was made with a combination of chrome and vegetable in a drum. I understand that the processes which followed the actual tannage were more or less conventional sole leather methods.

The stock out of the drum had a fair amount of draw in some of the softer areas of the bends, but by and large those were worked out in the rolling. Abrasion tests run on a Bureau of Standards machine in the laboratory at Graton & Knight, showed, to a great extent, superiority of that leather over straight vegetable tan. However, some of these tests were run during the war, and Graton & Knight did not go very much further with them at that time.

MR. LAUDER: It is my belief that no matter what type of tannage you carry out you will get this condition: Not only must you consider abrasion on the surface of the sole leather, but also you must consider the property of these fibers rubbing one against the other, wearing from the inside out.

It is my belief that you have to lubricate or cover these fibers in some way, or make these fibers so tough in the corium that when they do rub together they will outlast compound materials. I talked this matter over with Dr. Phillips of England when he was in Cincinnati, and his remarks were very encouraging along this line.

I have a method which I use on my leather-soled shoes whereby they outlast the compound materials two to one. It is a simple method. All I do is rub a thin commercial oil over the sole and over the heel of my shoes once a month. That is why I felt frustrated when I could not get leather soles and heels for my children's shoes anymore.

MR. KAY: Does that suggest that the wet wear of sole leather is due to the action of the water on the fiber? And that if you protect the tannage from the water, it will wear better?

MR. LAUDER: That is what I feel must happen. The oil when applied does give some degree of moistureproofing or wetproofing as well as some lubrication.

MR. KAY: There have been processes for improving wear by immersion in oil solutions. However, leathers so treated do not wear much better than the conventional leather. It is conceivable that the effect is only temporary—that excess oil can wash out—and therefore treatment has to be renewed along the lines you suggest. Does that make sense?

MR. LAUDER: Yes, it does make sense. If you add too much oil, you will be in difficulty because the fibers will separate from each other. Then you have too much lubrication.

DR. GEORGE VON FUCHS (Belmont, Mass.): During this entire meeting I have kept my peace. But now, when the question of oil adhesion to leather

fibers comes up, I have to speak. Oil—mineral oil, vegetable oil, or other oil—used in tanning has absolutely no affinity for leather. You have to have a coupling agent, and alkylated succinic acid has been found to provide that coupling agent. Two years ago at this meeting I spoke of a new way of lubricating leather. If Mr. Lauder would add a small amount of succinic acid to his shoes, he would not have to do it once a month, but it would be for the life of the shoe.

MR. KAY: Don't you think sulfonated oil acts as a coupling agent in conventional procedures?

DR. VON FUCHS: Unfortunately it also acts as an oil remover. It is hydrophilic. The same oil that you put on the fiber in the fatliquoring step will be floated off again when the leather becomes wet, the fibers will stick together, and the leather will dry hard.

MR. KAY: We had a paper at the beginning of the meeting indicating that sulfonated oi's are not removable.

DR. VON FUCHS: That is true, and that's just the trouble. They combine with the fiber but have no lubricating value of their own. They add to the fiber a certain degree of water affinity and actually increase the rate at which water will adhere and be absorbed. It has been shown by work done in East Germany that the so-called water-penetrating type of leather has that characteristic cumulatively increased by wetting and emulsifying agents. If you use a wetting agent in the degreasing followed by a wetting agent in the tanning and lubricating steps, followed by a wetting agent in the finishing process, the effect accumulates. On the other hand, if you use an agent which ties into the fiber and is also water-repellent, you have real permanent lubrication.

I described this phenomenon in this auditorium three years ago (*JALCA*, **52,** 550 [1957]) and subsequently gave a paper in Vienna on the subject, but the trouble was that we did not have a cheap enough compound. This condition has changed today.

MR. KAY: Do you find improved wear from that type of oiling?

DR. VON FUCHS: I have been using this process for ten years on my own soles, and it is good for the soles.

MR. WELDON: It is our responsibility to make as good a piece of leather as we can, and after we have made that piece of leather we must, as technical people, I firmly believe, exert all the power at our command to influence the

sales people and the customers. If we don't do that, we will go out of the picture. We must tie the two together—our technical know-how, which we demonstrate in the making of our leather, and salesmanship—which means we must also get out and help to sell it. You must have a combination of both if you are to be successful in the leather business today.

MR. BAILEY: Returning this conversation to chrome-retan technology—I wish to emphasize that there has been butyl-impregnated commercial chrome-retanned sole leather produced by the Van Tassel Leather Co. This product showed excellent durability and water resistance. This chrome-retan stock was comparable in wear to some of the very best of the composition rubber materials.

MR. KAY: Actually you do not have to go to chrome for that. If you take a minimum tannage—minimum in the sense of chemical stability—which you can obtain through pretannage, you can then impregnate with a great many materials to get physical properties which are desired. But you are still up against the problem that even if you build a better mousetrap, nobody will know about it unless people know that you have one. That is not our province.

CHAIRMAN WAGONER: This matter of wear in sole leather is a big feature, but it is confined largely to children's shoes and men's workshoes. Long wear, as Mr. Bailey was speaking about it, certainly is not a factor in our mode of living today, in the way that it was.

I am not entirely convinced that our best grades of vegetable-tanned sole leather are poor in wear. I think it was shown in the Camp Lee tests that actually in some cases the vegetable-tanned soles outwore composition soles. So, while I am not de-emphasizing wear in any way, I think that wear has to be put in its proper category. In the general use of sole leather there are many other factors that have to be given consideration.

One of the big ones is in their workability in the shoe factories, their flexibility, solidity, and things like that. We have got to be more flexible in the types of leather which we can produce.

That always brings up this question: Where are you going to do it? Can you do it in your tanning processes or finishing processes or in your beamhouse? That is one of the big advantages offered by the drum type of tannage, solvent tannages and things of that nature, whereby the time between preparing the hide and the tanning would be much shorter, and we would be able to control the properties much better. We have to make a certain amount of solid, firm leather, and yet out of the same piece of leather we are expected to cut a nice light, flexible woman's sole. And this has led to a great many treating processes that are carried out by cut sole operators. We do some of it our-

selves, and the shoe manufacturers do some. So, it is the possibility of being able to make different types of leather to meet the demands that needs to be given a lot of attention, and certainly this comfort factor is one to which all of us should direct a good bit of attention.

MR. KAY: That may be the opening we have been seeking: that, as an industry, we can, by judicious treatment, make a variety of leathers to meet the particular needs of the specific shoe manufacturer, which the synthetics people will find it exceedingly difficult to do. Their whole concept is based on mass production, just as ours has been. I think what I am saying is essentially what Mr. Wagoner said, that we have the possibility, by using these combinations of methods that we have discussed—drum tannages of various kinds, solvent tannages, and even conventional tannages (because there is still a place for that)—not only to survive but also to grow as an industry by becoming more flexible in our production. I wonder if anybody has given that some thought and is doing anything with that object in view.

CHAIRMAN WAGONER: I don't know of any comfort studies that are being made. Perhaps somebody else has something on that.

MR. PRESLEY: In regard to comfort, about three or four years ago some tests were run by an automotive company using upholstery leather versus the imitation. They put it on trucks traveling from New York to the West Coast. They used different types of upholstery leather, and various constructions and different types of imitations. They would juggle the drivers and then have them report as to the comfort they obtained from either one of the products. I don't think there was an official report on it, but in all cases the upholstery leather was superior to any of the plastics in comfort. Just how much can you sell comfort, however? You can talk about it, but will people buy it?

In regard to defects that are noticeable on upholstery leathers, in the last few years the Upholstery Leather Group through proper publicity has attempted to convince the buying public that they are the Hallmarks of Quality. There is a trend at the present time to recognize these facets.

I was only in the sole leather business a comparatively short time, but I have never been able to figure out why the purchasers of sole leather created such a furore about appearance and color. Where there may be slight oil stains and what-not, the sole leather tanner has to use all kinds of degreasing agents and bleaching assists just to turn out a pretty-looking piece of leather.

If the sole leather tanners had an opportunity to make the leather and leave the oil and natural greases in it, they still would have a better product as far as wear is concerned. But no, the tanner has to beat the leather up. And what does he have? Something slightly inferior, as far as I am concerned.

I think the buying public certainly needs a lot of education on this point, and that is where your sales people and publicity forces are going to have to go to work.

MR. KAY: I dispute your statement, Mr. Presley, or at least the implications. There is an old saying that the law is an ass, but it is still the law. If the customer demands clear leather, that is what we have to give him.

MR. PRESLEY: That is true, but why do we have to be pushed around that way?

MR. KAY: Because he is the boss.

DR. TURLEY: As a mere man, it is my observation that whenever the fair sex gets together in a game of bridge or for cocktails, one of the first things they do is to kick off their shoes. Why? If they were perfectly comfortable, they would not be aware of having shoes on. A lot could be done on that point, not only the materials but also the shoe construction.

In the Cincinnati meeting in 1953 Doctor Gaul, a foot specialist, gave a most alarming report. That should be good propaganda for us. He said that in trying to get a properly constructed shoe with porous construction he had found only one company in the United States where he could buy such a shoe.

MR. KAY: Don't you think this confirms exactly what I was saying? In this case women don't dress for comfort. They dress to please men.

DR. TURLEY: Let us make them comfortable at the same time.

DR. BUECHLER: I think you are wrong. Women dress to please other women.

MR. KAY: I bow to your greater experience, sir.

CHAIRMAN WAGONER: Gentlemen, we have covered quite a range of subjects here. We did a bit on chrome tanning, some fatliquoring, some nonfatliquoring, a little bit of merchandising, as well as vegetable tanning. All in all I think we have had a good discussion. If there are no other questions, I think we might close the session at this time.

Before doing so, I want to personally thank the members of the panel for their splendid cooperation in this symposium. To Arthur Kay, Dick Jones, Elwood Presley, and Allen Lauder, my sincere thanks. Also to Bob Kernahan and Tom O'Mara my thanks for handling the microphones so capably.

I would like to close this session with this thought: In our day-to-day operations of producing vegetable-tanned leather we should not forget that we also have a vital part in selling leather. We, in production, must constantly endeavor to produce the best quality leather that is possible at a realistic cost. Those of us who are charged with the technical phase of the industry must continually encourage and work toward developing more scientific knowledge of the process of converting hide into leather. We must endeavor to translate this knowledge to practical applications. We must strive to develop new means for measuring the quality of our leathers. We must learn more about how our leathers are used in the trade so as to meet their requirements better. We must furnish our principals and our promotion people with accurate physical and chemical data with which to help promote the sale of leather.

Through such efforts we, as tanners and leather chemists, can contribute greatly to expanding the use of leather—and in so doing to increasing the profits of our industry.